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OXYGEN RECLAMATION FROM CARBON DIOXIDE USING A SOLID OXIDE ELECTROLYTE

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Recently, Foster (1) reviewed some of the techniques which are being considered for reclaiming oxygen from expired carbon dioxide during prolonged space missions. One of the more promising concepts reviewed was the high-temperature electrolysis of carbon dioxide using a solid oxide electrolyte.

Some of the inherent advantages in using the solid oxide electrolyte system for oxygen recovery follow. Since only oxide ions can migrate through the solid electrolyte in an electric field, the separation of oxygen from the carbon dioxide in a sealed cell is excellent. No liquids are involved in the solid electrolyte system and therefore the problem of gas-liquid phase separation at zero-G is not encountered. Unlike fused salt electrolytes (2), the solid electrolyte is noncorrosive and therefore the number of materials that can be used for cell construction is less limited. The solid electrolyte system can be used continuously for the electrolysis of either carbon dioxide or water vapor or a mixture of the two gases.

The recent progress (3,4) made in the application of the solid electrolyte concept toward the development of an oxygen generator for space will be presented. Progress has been made in both the fabrication and extended operational performance of carbon dioxide electrolyzers utilizing disk-shaped solid electrolytes. Advances which have been made in the technology of electrolyte fabrication, in the formulation and application of gas-tight high-temperature sealants, and in electrode preparation will be discussed.

EXPERIMENTAL

Details of electrolyte fabrication, electrode application and sealant preparation can be found elsewhere (3,4).

RESULTS AND DISCUSSION

The most serious disadvantage in using a solid oxide electrolyte system for the electrolysis of carbon dioxide is that a high temperature (~1000°C) is generally required to maintain a high Faradaic efficiency for oxygen generation (>95%). High-temperature operation poses problems in terms of materials for sealants and cell structures, power for maintaining the high temperature, increased cell weight and volume required for insulation, and reliability. Therefore, it is desirable to operate at lower temperatures if a high Faradaic efficiency can be maintained and electrolysis power requirements are not excessive because of higher cell resistances at lower temperatures.

In this research we have been able to operate at a high oxygen Faradaic efficiency below 1000°C. Experiments were normally conducted near 850°C at current efficiencies approaching 100%. The ability to achieve high Faradaic efficiencies at these lower temperatures was due primarily to

the presence of small amounts of water vapor introduced into the carbon dioxide feed gas to act as a catalyst for the cathode reaction (5).

Table 1 shows the test results of a long-duration electrolysis experiment using a 1-amp,

TABLE 1. PERFORMANCE OF 1-AMP ELECTROLYZER WITH GLASS CERAMIC SEAL DURING 1128-HR LIFE TEST

Time, hr	Temp., °C	CO ₂ flow, ml/min	Cell voltages, ^b V		Cell resistances, ^c ohms		C.E. O ₂ , %
			No. 1	No. 2	No. 1	No. 2	
0	857	140	3.80	3.55	5.25	4.50	98.5
2.5	857	140	4.05	3.69	9.6 ^d	---	98.5
29.2	845	140	4.35	3.92	---	---	94.5
92	845	140	4.59	4.23	6.88	6.00	95.0
94	858	130	4.35	4.01	6.39	5.65	99.0
95	858	63	4.36	4.03	---	---	97.5
125	858	57	---	4.08	---	---	91.6
125.5	858	77	---	4.10	---	---	93.7
191	---	75	4.66	4.32	---	---	94.7
263	---	71	4.80	4.42	---	---	96.3
294	---	83	9.44 ^d	---	---	---	98.7
456	858	87	5.18	4.70	8.0	7.1	99.5
600	858	80	5.36	4.81	---	---	97.4
797	858	78	10.08 ^d	---	---	---	96.7
1011	858	73	5.59	4.84	8.6	7.2	96.1
1128	857	80	6.94	5.50	11.0	8.4	97.5

^aArea of each electrode = 5 cm²; thickness of each disk = 1.15 mm; electrolysis current = 500 mA per cell.

^bThe resistance of the leads to each cell was approximately 1.5 ohms resulting in a voltage drop of 0.75 V per cell or 1.50 V for the two cells in series. These values have not been subtracted from the voltages given in the table.

^cIn addition to the 1.5 ohms per cell of (b), the leads to the impedance bridge add 0.3 ohm. Thus, 1.8 ohms per cell or 3.3 ohms for the two cells in series should be subtracted from the resistance shown in the table.

^dValue for both cells in series.

two-disk CO₂ electrolyzer. During the test, carbon dioxide saturated with water vapor at room temperature (~25°C) was fed into the quartz envelope (Figure 1) and oxygen was generated at the

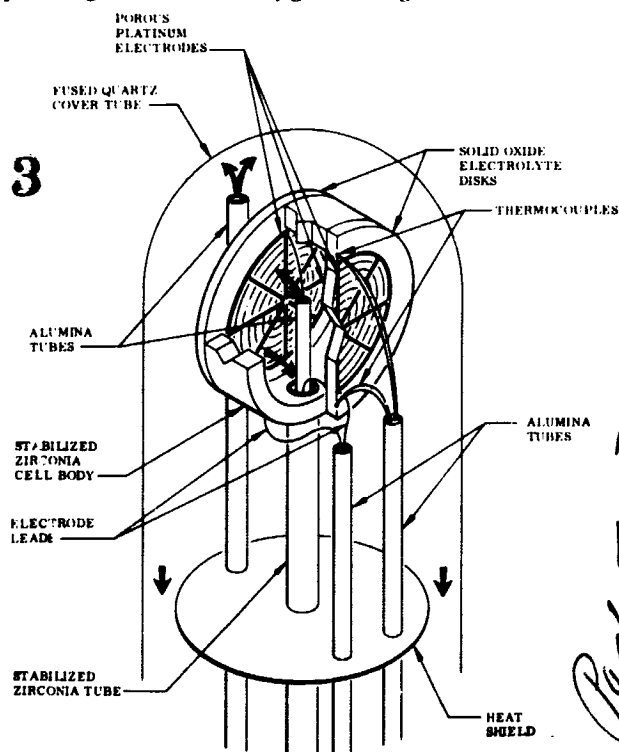


FIGURE 1. 1-AMP SOLID OXIDE ELECTROLYTE CARBON DIOXIDE ELECTROLYZER

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anodes located in the interior of the lollipop. The electrolyte composition for this experiment was $(\text{ZrO}_2)_{0.85}(\text{CaO})_{0.15}$ and the sealant was magnesium aluminum silicate. The current density was maintained at 100 mA/cm² for a total current of 500 mA/cell. The two cells were connected electrically in series. It is apparent from table 1 that the oxygen current efficiency remained near 100% although the cell resistance increased with decreasing CO₂ flow rate. This suggested that the cathodes were starved for CO₂ as a result of the large volume of the quartz envelope and the relatively low gas-flow rate. Therefore, in subsequent experiments carbon dioxide was fed to the inside of the lollipop and the interior electrodes were made the cathodes.

After termination of the 1128-hour life test the 1-amp battery was disassembled and examined. Photomicrographs revealed that the sealant had penetrated the electrolyte and cell body. The seal areas of the disks were greatly weakened, indicating that the magnesium aluminum silicate sealant would be unsuitable for long-term reliable operation even though the sealant withstood 1128 hr of operation.

Further experiments were conducted with another 1-amp unit containing a gold metal seal instead of a magnesium aluminum glass-ceramic seal; in addition, the carbon dioxide was fed to the inner chamber of the lollipop and not into the quartz envelope. The performance of this unit during a 2016-hour test is summarized in table 2.

TABLE 2. PERFORMANCE OF 1-AMP ELECTROLYZER WITH PRECIOUS METAL SEAL DURING 2016-HR LIFE TEST

Time, hr	Temp., °C	CO ₂ flow, ml/min	Cell voltages, ^b V		C.E.O ₂ , %
			No. 1	No. 2	
0	853	24	3.40	3.17	100
17	853	16.7	3.13	2.96	97.6
18	853	21.8	3.08	2.91	97.6
24	853	20.5	3.10	2.94	96.5
48	853	22.9	3.21	2.94	98.1
185	853	21.6	3.21	3.00	96.0
335	852	20.5	3.23	3.04	97.9
550	852	19.9	3.29	3.09	96.6
1001	850	20.6	3.43	3.23	97.4
1362	848	19.3	3.61	3.39	94.7
1436 ^c	853	19.6	3.49	3.25	94.2
1436 ^d	852	19.7	3.55	3.31	96.3
1584	852	19.6	3.58	3.29	97.5
2016	852	19.7	3.74	3.39	97.8

^aArea of each electrode = 5 cm²; thickness of disks: No. 1 = 1.3 mm, No. 2 = 1.1 mm; electrolysis current = 500 mA per cell.

^bThe lead resistance of approximately 1.5 ohms gives a voltage drop of 0.75 V per cell which has not been subtracted from the values shown here.

^cThe unit was shut down after 1436 hr of operation because of a planned interruption in laboratory power.

^dAfter being off for five days, the unit was placed back in operation.

The oxygen Faradaic efficiency was again near 100%, but unlike the previous run the applied voltage did not increase with time at constant current. No visible degradation of this unit was apparent at the completion of the extended test and the unit remained in working condition.

It is of interest to determine what portion of the total applied cell voltage could be attributed to IR drops or ohmic losses, polarization and theoretical cell voltage. This was done for cell No. 1, table 2, after 18 hr of operation. The breakdown in the voltage is as follows:

IR drops = 1.15 V, polarization = 0.28 V, and theoretical cell voltage = 0.90 V. It is apparent from the foregoing that ohmic losses account for most of the voltage higher than theoretical in the cell. Ohmic losses can be reduced significantly by reducing the electrolyte thickness. No emphasis was placed on fabricating thin electrolytes in this work.

Based on the results of the extended tests, the following conservative design parameters for a one-man prototype CO₂ electrolyzer seem reasonable at the present time: operating temperature, 850°C; current density, 100 mA/cm²; O₂ Faradaic efficiency, ~100%, and an electrolysis power efficiency, ~50%.

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